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APPLICATION OF THE UREY-BRADLEY AND THE ORBITAL VALENCY FORCE FIELDS TO SOME TETRAHEDRAL IONS

T. A. HARIHARAN

DEPARTMENT OF PHYSICS, REGIONAL ENGINEERING COLLEGE, SURATHKAL, MYSORE STATE

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ABSTRACT. In the case of the tetrahedral ions $CrO_4^{=}$, $MoO_4^{=}$, $GaBr_4^{-}$, $InBr_4^{-}$ and $TlBr_4^{-}$ the force constants have been calculated using the Urey-Bradley type of potential function and the orbital valency force field. The appropriate potential function for each case is discussed.

INTRODUCTION

Among the various types of potential functions used for studying the problem of molecular vibrations the valence force function is more extensively adopted than the others. Instead of a simple valence force function containing only quadratic terms, the one which takes into account the various interaction terms is found to be more satisfactory. However, a proper choice of these interaction terms or their adequate physical interpretation is not quite simple. A modification of the valence force function has been brought about by Urey and Bradley (1931) by introducing repulsion terms between non-bonded atoms of the type a/R^n where 'a' and 'n' are constants and R the distance between the atoms. A systematic investigation by Heath and Linnet (1948) on a number of tetrahedral halides of the group IV elements revealed that in a majority of cases n comes out to be nearly 4.5. This value was not acceptable for two reasons : (a) for the value $n = 4.5$ the stretching of the bonds would be more than what has been actually observed, (b) the Lennard-Jones (1924) relation $V = a/R^{12} - b/R^6$, for the inert gas atoms are more reasonable because the bonded halogen atoms resemble electronically the inert gas atoms. According to the Lennard-Jones function, n can be taken as 12 after neglecting the second term which corresponds to attraction and is small compared to the first term. The potential function consists of four constants, namely, the stretching constant K_1, the bending constant K_α, $A\left(=\frac{1}{2}\frac{d^2V}{dR^2}\right)$ and $\frac{B}{R}\left(=-\frac{1}{R}\frac{dV}{dR}\right)$ where V is the function mentioned above. The relation between A and B/R becomes fixed for any particular value of n, i.e., $A: B/R = n+1: 2$.

Another modification of the simple valence force field is what is known as the orbital valence force field first introduced by Heath and Linnet (1948). The

main feature of this function is that it makes use of the same constant for both the in plane and out of plane vibrations in the case of planar molecules and it differs from the simple valency force field only in its treatment of angular vibrations. According to Pauling's (1931) idea of directed valency the orbitals of an atom are set at definite angles to each other and the most stable bond between two atoms, say P and Q, is formed when one of the bond forming orbital of P overlaps to a maximum extent the bond forming orbitals of Q. Whenever there is a displacement from the maximum overlap during molecular vibrations restoring forces will be called into play and these can be assumed to be proportional to the displacements (which are of course small) if the vibrations are simple harmonic.

There are two ways by which the overlap of the bond forming orbitals can be increased during the vibrations. In the case of tetrahedral molecules or ions with which we are concerned here the orbitals of the central atom might be rotated as a whole in such a way as to improve the overlap. On the other hand, the orbitals of the central atom might change their hybridisation ratios by changing the angles at which they are set with each other so as to follow the movements of the outer atoms. This idea has been called orbital following.

The orbital valency force field without taking into account the idea of orbital following also consists of four constants K_1, K_α' (instead of K_α as in the simple valency force field), A and B/R. Heath and Linnet (1948) have observed that for the ions ClO_4^-, $SO_4^=$, $SeO_4^=$ and $PO_4^{\equiv}$ the orbital valency force field is quite satisfactory. Such a force field is assumed in the present investigation to evaluate the force constants of the ions $CrO_4^=$, $MoO_4^=$, $GaBr_4^-$, $InBr_4^-$ and $TlBr_4^-$.

THE POTENTIAL ENERGY FUNCTION

The potential energy function for tetrahedral molecules XY_4 can be written in the form

$$U = \sum_i f(r_i) + \sum_{i,j} F(R_{ij}) + \sum_{i,j} \tfrac{1}{2} K_\alpha (\Delta\alpha_{ij})^2 \qquad \ldots \quad (1)$$

the first term arising due to change in the $X-Y_i$ distance (r_i), the second term due to changes in the Y_i-Y_j distance (R_{ij}), and the last term due to changes in the angles $Y_iXY_j(\alpha_{ij})$. For small values of these variations the functions $f(r_i)$ and $F(R_{ij})$ can be expanded in powers of r_i and R_{ij} which denote the changes in r_i and R_{ij} from their equilibrium values r_i° and R_{ij}°. Retaining powers only up to the second we have

$$U = \sum_i f(r_i^0) + \sum_i f'(r_i^0)\Delta r_i + \sum_i \tfrac{1}{2} f''(r_i^0)\Delta r_i^2$$
$$+ \sum_{i,j} F(R^0{}_{ij}) + \sum_{i,j} F'(R_i^\circ)\Delta R_{ij} + \sum_{i,j} \tfrac{1}{2} F''(R^0{}_{ij})\Delta R^2{}_{ij} + \sum_{i,j} \tfrac{1}{2} K_\alpha (\Delta\alpha_{ij})^2 \quad \ldots \quad (2)$$

Taking into consideration the above type of potential function the equations for the frequencies can be written as

I For the simple valency force field :

Type A_1 $$\lambda_1 = \mu_y(K_1+8A) \quad \ldots (3)$$

Type T_2

$$\lambda_2+\lambda_3 = (\mu_y+\tfrac{4}{3}\mu_x)\left(K_1+\tfrac{8}{3}A-\tfrac{4}{3}\frac{B}{R}\right) +(\mu_y+\tfrac{8}{3}\mu_x)\left(2K_\alpha+\tfrac{4}{3}A+\tfrac{10}{3}\frac{B}{R}\right)$$

$$-\tfrac{8}{3}\mu_x\left(\tfrac{8}{3}A-\tfrac{4}{3}\frac{B}{R}\right) \quad \ldots (4)$$

$$\lambda_2\lambda_3 = (\mu_y{}^2+4\mu_x\mu_y)\left[(K_1+\tfrac{8}{3}A-\tfrac{4}{3}\frac{B}{R}\right)$$

$$\left(2K_\alpha+\tfrac{4}{3}A+\tfrac{10}{3}\frac{B}{R}\right)-\tfrac{1}{2}\left(\tfrac{8}{3}A-\tfrac{4}{3}\frac{B}{R}\right)^2\Big] \quad \ldots (5)$$

Type E. $$\lambda_4 = \mu_y\left(3K_\alpha+2A+\frac{B}{R}\right) \quad \ldots (6)$$

II For orbital valency force field :

Type A_1 $$\lambda_1 = \mu_y(K_1+8A) \quad \ldots (7)$$

Type T_2

$$\lambda_2+\lambda_3 = (\mu_y+\tfrac{4}{3}\mu_x)\left(K_1+\tfrac{8}{3}A-\tfrac{4}{3}\frac{B}{R}\right)$$

$$+(\mu_y+\tfrac{8}{3}\mu_x)\left(K'_\alpha+\tfrac{4}{3}A+\tfrac{10}{3}\frac{B}{R}\right)$$

$$-\tfrac{8}{3}\mu_x\left(\tfrac{8}{3}A-\tfrac{4}{3}\frac{B}{R}\right) \quad \ldots (8)$$

$$\lambda_2\lambda_3 = (\mu_y{}^2+4\mu_y\mu_x)\left[\left(K_1+\tfrac{8}{3}A-\tfrac{4}{3}\frac{B}{R}\right)\right.$$

$$\left.\left(K_\alpha{}'+\tfrac{4}{3}A+\tfrac{10}{3}\frac{B}{R}\right) -\tfrac{1}{2}\left(\tfrac{8}{3}A-\tfrac{4}{3}\frac{B}{R}\right)^2\right] \quad \ldots (9)$$

Type E $$\lambda_4 = \mu_y(K_\alpha{}'+2A+\frac{B}{R}\right) \quad \ldots (10)$$

μ_x and μ_y denote the reciprocal of the masses of the atoms X and Y respectively and $\lambda_i = 4\pi^2 c^2\nu_i{}^2$. If the interaction function between non-bonded-atoms is assumed as $V = a/R^n$

then $$\frac{B}{R^0} = \frac{na}{(R^0)^{n+2}} \qquad \text{and } A = \frac{n(n+1)a}{2(R^0)^{n+2}}$$

so that $$\frac{A}{(B/R^0)} = \frac{n+1}{2}$$

EVALUATION OF THE CONSTANTS

The values of K_α and K_α' can be obtained in terms of A from the equation for the doubly degenerate frequency λ_4. These can be then stustituted in the first equation for the triply degenerate vibrations T_2 which will give an equation in K_1 and A which can be solved simultaneously with the equation for the totally symmetric class A_1. By substituting the values of the force constants in the second equation for T_2, the calculated and observed values of $\lambda_2\lambda_3$ can be compared.

RESULTS

The fundamental frequencies of the ions are taken from the published results on their Raman spectra and they are given in Table I. In Table II to V the values of the force constants for the six ions have been given while Table VI contains the observed and calculated values of $\lambda_2\lambda_3$. All the force constants are given in 10^5 dynes/cm.

TABLE I

Frequencies in cm^{-1}

Ion	$\nu_1(A_1)$	$\nu_2(T_2)$	$\nu_3(T_2)$	$\nu_4(E)$	Reference
$CrO^{=}_4$	858	510	875	485	Landolt Bornsteins's
$MnO^{=}_4$	940	365	895	220	Tables, 1953
$GaBr^{=}_4$	210	102	278	71	Woodward and Nord, (1955)
$InBr^{=}_4$	197	79	239	55	Woodward and Bill, (1955)
$TlBr^{=}_4$	190	64	209	51	Rolfe, Sheppard and Woodward (1954)

TABLE II

S.V.F.F. n = 4.5

Ion	K_1	A	B/R	K_α
$CrO^{=}_4$	4.209	0.3416	0.1242	0.4703
$MoO^{=}_4$	5.503	0.3536	0.1286	0.0634
$GaBr^{=}_4$	1.269	0.101	0.0367	−0.0004
$InBr^{=}_4$	1.307	0.0654	0.0237	−0.004
$TlBr^{=}_4$	1.26	0.055	0.02	−0.0024

TABLE III

S.V.F.F. n = 12

Ion	K_1	A	B/R	K_α
$CrO_4^{=}$	4.466	0.3095	0.0476	0.517
$MoO_4^{=}$	5.73	0.3252	0.05	0.1085
$GaBr_4^{=}$	1.054	0.1278	0.0197	−0.0126
$InBr_4^{=}$	1.365	0.058	0.009	0.0058
$TlBr_4^{=}$	1.303	0.0495	0.0076	0.0053

TABLE IV

O.V.F.F. n = 4.5

Ion	K_1	A	B R	K_α'
$CrO_4^{=}$	3.50	0.43	0.1564	1.201
$MoO_4^{=}$	5.408	0.3654	0.1328	0.1623
$GaBr^{=}_4$	1.269	0.1009	0.0367	−0.0011
$InBr^{=}_4$	1.313	0.0646	0.0235	−0.012
$TlBr^{=}_4$	1.263	0.0545	0.0198	−0.0063

TABLE V

O.V.F.F. n = 12.

Ion	K_1	A	B/R	K_α'
$CrO_4^{=}$	3.741	0.4	0.0615	1.3568
$MnO_4^{=}$	5.581	0.3438	0.0529	0.2856
$GaBr_4^{=}$	1.345	0.0915	0.014	0.0404
$IdBr_4^{=}$	1.357	0.059	0.009	0.0153
$TlBr_4^{=}$	1.296	0.0504	0.0078	0.0139

TABLE VI

Ion	$\frac{\lambda_2\lambda_3}{\mu_y^2+4\mu_x\mu_y}$ observed	$\frac{\lambda_2\lambda_3}{\mu^2_y+4\mu_x\mu_y}$ calculated S.V.F.F. n = 4.5	S.V.F.F. n = 12	O.V.F.F. n = 4.5	O.V.F.F. n = 12
$CrO^{=}_4$	7.936×10^{10}	8.691×10^{10}	8.105×10^{10}	9.754×10^{10}	9.41×10^{10}
$MoO^{=}_4$	5.692×10^{10}	6.146×10^{10}	5.017×10^{10}	6.461×10^{10}	5.557×10^{10}
$GaBr^{=}_4$	3.195×10^{9}	3.573×10^{9}	2.391×10^{9}	3.755×10^{9}	3.033×10^{9}
$InBr^{=}_4$	2.085×10^{9}	2.1948×10^{9}	1.693×10^{9}	2.117×10^{9}	1.763×10^{9}
$TlBr^{=}_4$	1.545×10^{9}	1.792×10^{9}	1.379×10^{9}	1.761×10^{9}	1.444×10^{9}

It can be seen from Table VI that in the case of MoO_4 $GaBr_4$ and $TlBr_4$ the orbital valency force field field with $n = 12$ is more satisfactory than the others while for $InBr_4$ the same field with $n = 4.5$ instead of 12 suits better. For the chromate ion the simple valency force field with $n = 12$ yields better results than the others. This simple valency force field with $n = 4.5$ is least satisfactory for all the ions. In the case of the ions ClO^{-}_4, $SO^{=}_4$, $SeO^{=}_4$ and $PO_4^{\equiv}$, Heath and Linnet (1948) have observed that the orbital valency force field holds better. The difference between observed and calculated values of $\lambda_2\lambda_3$ can be further reduced by in- troducing modifications such as orbital following.

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